numerically very much like those given by the Jones theory. It is pointed out, however, that the sum of the contributions from all states could be very much different. Two other factors tending to change the axial ratio were found, one of which, the exchange stress, could be appreciable. A rough estimate made of the "effective stress" in beryllium was of the right order of magnitude.

The second investigation concerned the change of the lattice parameters with alloying. It was found that the change in axial ratio with alloying is due to a different mechanism from that proposed by Jones. However, use of the effective-mass theory allowed us to establish a connection between the band structure and the change in axial ratio when the correct mechanism is taken into account. It is remarkable that using the correct method, we draw the same qualitative conclusions concerning band structure as does Jones! It may be necessary to use a more sophisticated method in order to obtain numerical agreement with experiment, but the effective-mass treatment doubtlessly contains the essential physics. Thus, the most attractive feature of the Jones theory remains, i.e., the possibility of getting information about the band structure from the alloying data.

In the course of the first investigation a formalism was developed which is capable of giving the first-order effect of a homogeneous deformation on the energy band structure. Several possible applications of such a formalism were mentioned in Sec. 4.

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Properties of Germanium Doped with Nickel

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The temperature dependence of electrical resistivity in p- and n-type nickel-doped germanium crystals indicates that nickel introduces two acceptor levels in germanium at 0.22 ± 0.01 ev from the valence band and 0.30 ± 0.02 ev from the conduction band. Ionization energies deduced from infrared photoconductivity studies at 77°K are in agreement with the values obtained from resistivity measurements. N-type samples show higher photosensitivity than p-type samples and demonstrate quenching effects. The distribution coefficient for nickel in germanium is about 2.3×10^{-6}.

I. INTRODUCTION

This paper presents measurements of electrical and optical properties of germanium crystals containing nickel as the major impurity. Results are similar in most respects to those reported previously for Fe-doped[1,2] and Co-doped[3] germanium crystals. In a paper primarily concerned with the effects of Ni and Cu on carrier lifetime in germanium, Burton *et al.*[4] have reported low-temperature conductivity and Hall coefficient data which indicated that Ni introduces an acceptor level at about 0.23 ev from the valence band of germanium. This conclusion is confirmed. In addition, evidence is presented indicating that Ni introduces another acceptor level at about 0.30 ev from the conduction band. A summary is given comparing the properties of Fe-, Co-, and Ni-doped germanium crystals.

II. EXPERIMENTAL RESULTS

A. Crystal Preparation

The methods of crystal growth and sample preparation used with Ni-doping experiments were similar to those used in previous work with Fe- and Co-doping.[1,3] Experimental techniques used in studying the Ni-doped samples have also been described.[1,2]

Johnson Matthey Company (JM) "spectroscopically pure" Ni and Sigmund Cohn (SC) "chemically pure" Ni were used for doping. Initial experiments using the JM Ni indicated that about 10 percent of the carriers introduced into the Ge crystals as a result of doping were probably due to low ionization energy acceptor impurities in the Ni. The SC Ni proved somewhat more satisfactory either because of a lower concentration of specific low ionization energy acceptor impurities or because acceptor impurities were compensated by donor impurities. Spectroscopic analyses of both sources of Ni indicated "barely detectable" amounts of B and "traces" of Al. The SC Ni analysis also indicated a

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[1] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954).
[2] R. Newman and W. W. Tyler, Phys. Rev. **96**, 882 (1954).
[3] Tyler, Newman, and Woodbury, Phys. Rev. **97**, 669 (1955).
[4] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).

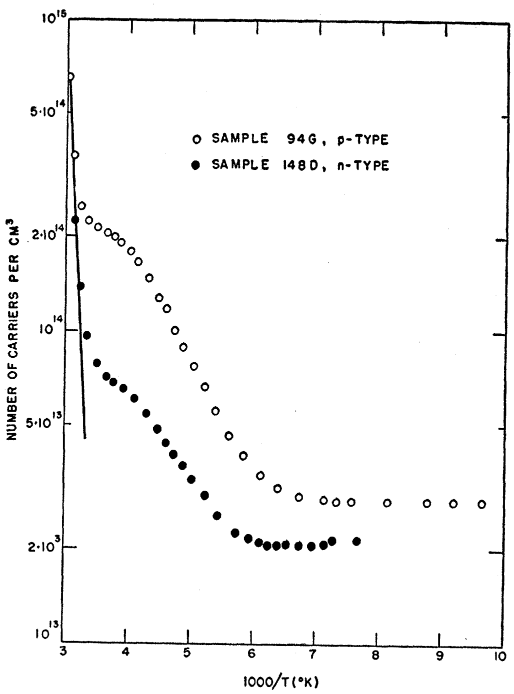

FIG. 1. Temperature dependence of carrier concentration for low-resistivity n- and p-type Ni-doped crystals. (On the ordinate, $2 \cdot 10^3$ should be $2 \cdot 10^{13}$.)

"slight trace" of Ga.[5] In an attempt to decrease the concentration of these acceptor impurities, single crystals of Ni were grown using the SC Ni as raw material. Comparative spectrographic analyses were made of the starting material and a third generation Ni crystal grown from central portions of preceeding crystals. There was no evidence of significant reduction of the B, Al, or Ga content from spectroscopic analyses or from doping experiments.

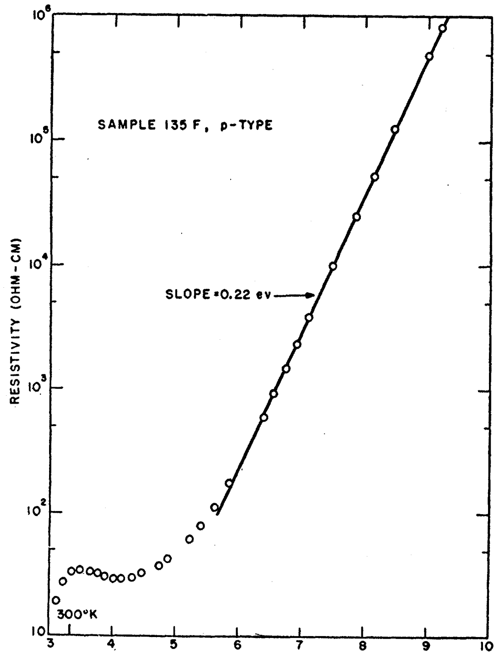

FIG. 2. Resistivity vs reciprocal temperature for a high-resistivity p-type Ni-doped Ge crystal (sample 135F).

Subsequent to initial doping experiments which indicated the presence of low-ionization-energy acceptor impurities in the Ni, all crystals were grown with small amounts of dilute As-Ge or Sb-Ge alloys added to the melt to compensate acceptor impurities. Because of their greater homogeneity, the most satisfactory counter-doping alloys for this purpose are Ge single crystals grown with suitable As- or Sb-doping. In searching for acceptor levels other than the 0.22-ev level, sufficient amounts of counter-doping donor alloy were used to fill the 0.22-ev levels in addition to compensating acceptor impurities. By such methods p- and n-type samples were obtained which showed temperature dependence of resistivity characteristic of levels at 0.22 ev from the valence band and 0.30 ev from the conduction band. All of the Ni-doped samples studied could be placed in one of four categories, consistent with the two-acceptor model. Assume N Ni atoms per cm³, p holes per cm³ due to the acceptor impurities in the Ni, and n electrons per cm³ from the counter-doping alloy. If $n-p<0$, the sample is low-resistivity p-type. Due to freeze-out of the holes supplied by Ni atoms, the resistivity first rises on lowering the temperature but becomes limited by the low-ionization-energy ac-

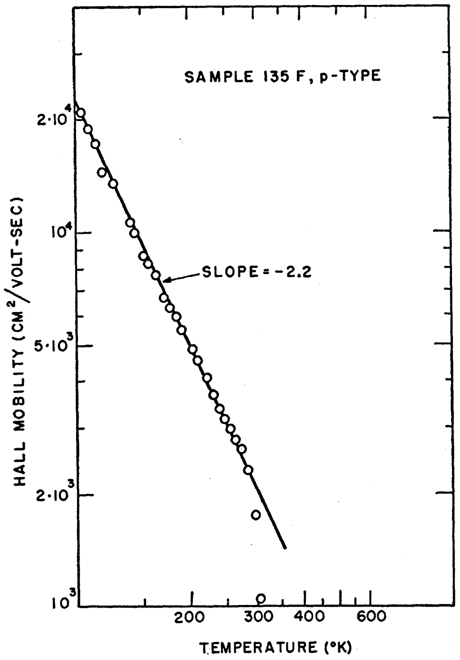

FIG. 3. Hall mobility vs temperature for p-type Ni-doped Ge crystal (sample 135F).

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[5] The Ni used was supplied by D. L. Martin. All spectroscopic analyses were made by L. B. Bronk.

ceptor states. If $0<n-p<N$, the sample is high-resistivity p-type and shows a temperature dependence of resistivity characteristic of the lower Ni acceptor state. If $N<n-p<2N$, the sample is high-resistivity n-type and shows a temperature dependence of resistivity characteristic of the upper Ni level. For $2N<n-p$, a low-resistivity n-type sample is observed with the resistivity rise limited by excess low-ionization-energy donors.

B. Electrical Properties

Figure 1 shows plots of number of carriers *vs* reciprocal temperature for Ni-doped Ge crystals characteristic of the first and last categories described above. The number of carriers was obtained from the Hall coefficient using the relation $R_H=1/ne$. From these curves, values of N can be obtained and estimates made of the effective distribution coefficient for Ni in Ge. Values obtained are 2.4×10^{-6} for sample 94G and 2.2×10^{-6} for sample 148D. These values are about a factor of 2 lower than the value given by Burton *et al.*[4] The principal source of error for the values given above is lack of exact knowledge of the concentration of Ni in the melt during crystallization of the sample. The effective distribution coefficient may also depend to some extent on the concentration of Ni in the melt, on rate of crystallization and rate of cooling after crystallization. For 94G, the concentration in the melt was 1.9×10^{-3} and for 148D about 5.7×10^{-4}. In each case the rate of crystallization was about 1.4 grams per minute. The agreement between values of effective distribution coefficient for these p- and n-type crystals indicates that the number of upper acceptor levels introduced by Ni is equal to the number of lower levels within experimental error.

Figures 2 and 3 show the temperature dependence of resistivity and mobility for a high-resistivity p-type Ni-doped sample. Eight such p-type samples from these different crystals were studied. Energy values given by the slopes of resistivity *vs* reciprocal temperature range from 0.21 ev to 0.23 ev. Figures 4 and 5 show similar curves for a high-resistivity n-type Ni-doped sample. Six such samples from six different crystals were studied. Energy values range from 0.28 ev to 0.31 ev.

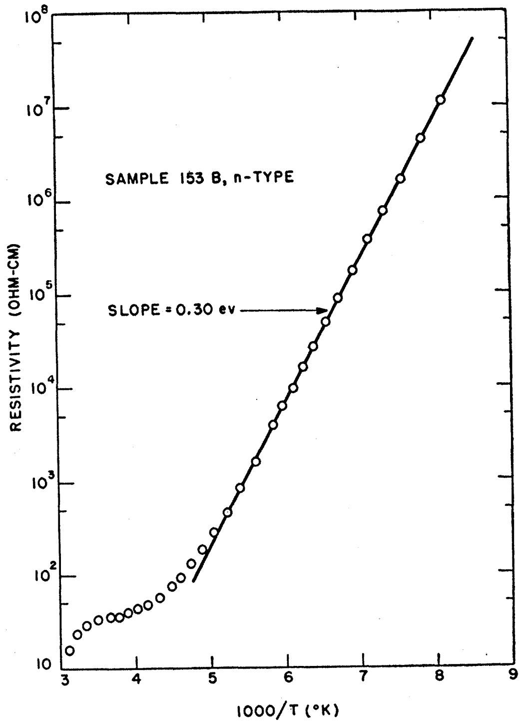

Fig. 4. Resistivity *vs* reciprocal temperature for a high-resistivity n-type Ni-doped Ge crystal (sample 153B).

The temperature dependence of Hall mobility shown in Figs. 3 and 5 is not typical of all the samples studied. In many high-resistivity Ni-doped samples, particularly for n-type samples, anomalous Hall mobility effects were observed. Figure 6 shows measured mobility data for high-resistivity n- and p-type samples 152A and 142I. Resistivity data for these samples showed the characteristic energies of 0.30 ev and 0.23 ev, respectively, throughout the temperature range studied. The anomalous mobility behavior generally becomes pronounced at temperatures below 200°K. Very few high-resistivity samples showed well-behaved mobility down to 100°K. In some cases the measured mobility values would break from the normal linear relationship and become relatively independent of temperature; in other cases mobility values would fall very rapidly after breaking from the normal relationship, sometimes

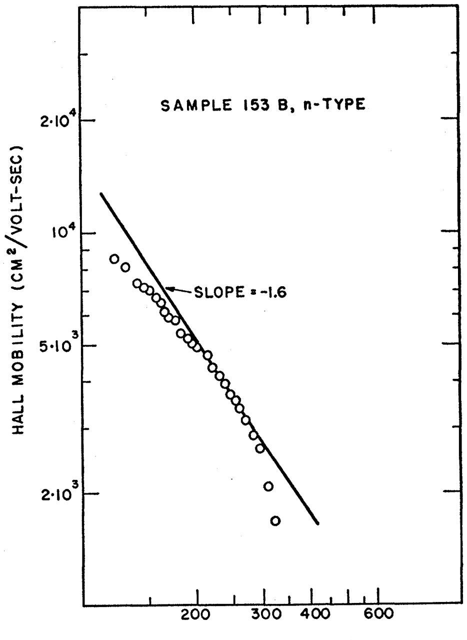

Fig. 5. Hall mobility *vs* temperature for n-type Ni-doped Ge crystal (sample 153B).

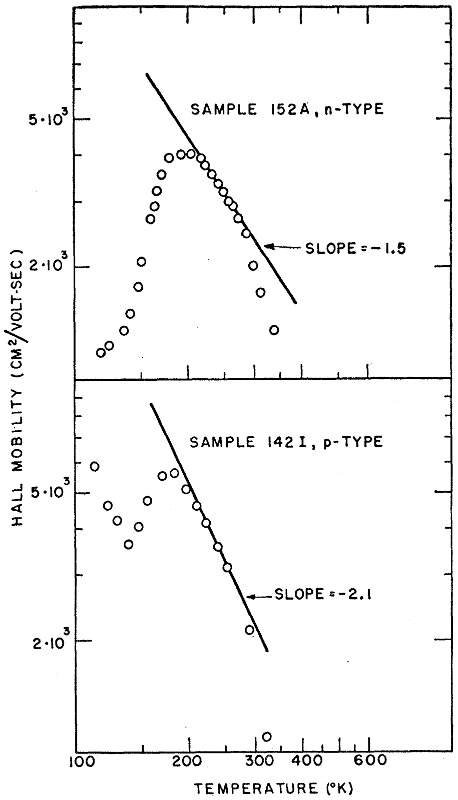

FIG. 6. Anomalous Hall mobility of high-resistivity n- and p-type Ni-doped Ge crystals (samples 152A and 142I).

falling several decades in a temperature interval of 30 to 40°K. Anomalous mobility behavior observed in high-resistivity Ni-doped samples is thought to be due to macroscopic potential variations which develop as the samples are cooled. Resistivity may not rise uniformly throughout the sample and small disconnected regions in the sample may actually remain at a relatively low resistivity level.

C. Photoconductivity

Infrared photoconductivity studies at 77°K were made on p-type samples from three different crystals and on n-type samples from three different crystals. Figures 7 and 8 show the spectral dependence of photoconductivity for typical p- and n-type samples. The curves are qualitatively similar to those reported previously for Au[6]-, Fe[2]-, and Co[3]-doped Ge crystals. In the region of impurity photoconduction the photosensitivities of n- and p-type Ni-doped samples were comparable. In the region of intrinsic absorption ($h\nu > 0.7$ ev), n-type samples were a factor of 10 to 10^2 more photosensitive than p-type samples. Quenching effects in n-type samples were observed. Maximum quenching effects occurred at about 0.5 ev with observed decreases in background photoconduction of about 50 percent. The spectral dependence of photoconduction in either p- or n-type samples was very reproducible from sample to sample and seemed independent of mobility behavior. Anomalous mobility behavior presumably affects the magnitude but not the spectral dependence of photoconduction in samples which are all of one type. For one Ni-doped sample, a spectral response was observed which behaved like n-type material from 0.70 to 0.45 ev and showed the characteristic p-type spectrum from 0.45 to 0.22 ev. Careful probing studies in the dark at low temperature subsequently confirmed that this sample was of mixed type.

Room-temperature lifetime measurements were made on many of the Ni-doped samples. Lifetime values were obtained from the rate of photoconductivity decay after spark excitation. Samples grown from a melt containing about 0.08 atomic percent Ni with hole concentrations of about 10^{14} per cm^3 indicated carrier lifetime of several microseconds or less. The results are qualitatively similar to those of Burton *et al.*[4]

III. SUMMARY AND DISCUSSION

Table I presents a summary of impurity levels in Ge crystals which have been identified with the presence of Fe, Co, and Ni impurities in the melt. Approximate values for effective distribution coefficients have also been listed. E_{vi} represents energy measured from the valence band to the impurity level in p-type samples; E_{ci} is measured from the impurity level to the conduction band in n-type samples. The experimental error

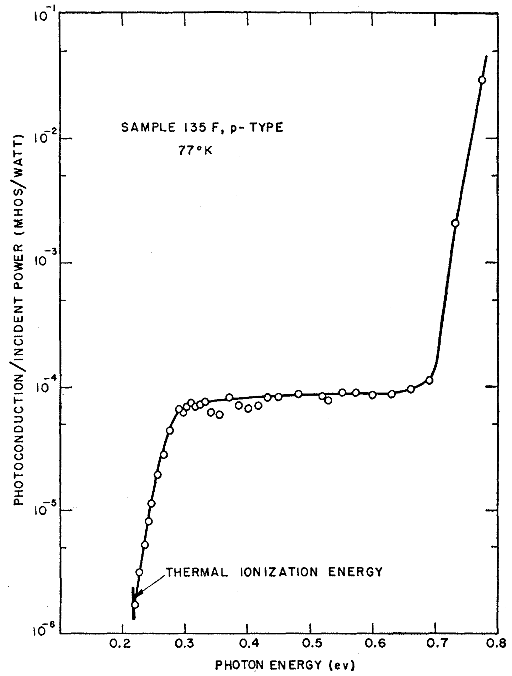

FIG. 7. Photoconductive spectrum of a p-type Ni-doped Ge crystal at 77°K (sample 135F).

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[6] R. Newman, Phys. Rev. 94, 278 (1954).

in determining slopes of resistivity plotted against reciprocal temperature, from which the energy values of impurity levels were obtained, is ±0.02 ev at most. The use of resistivity data rather than Hall coefficient data in determining energy values is somewhat arbitrary. According to the simple theory that leads to a 3/2 power dependence of mobility on temperature, the dependence of mobility on temperature cancels the theoretical change in effective density of states with temperature, justifying the use of resistivity data in determining energy values. The mobility does not follow the 3/2 power law in *p*-type material but correction of energy values to account for this would raise the quoted E_{vi} values by only about 0.01 ev. Such corrections have not been carried out because experimental and theoretical uncertainties in interpretation of the data are comparable in magnitude. No information has been obtained showing possible temperature dependence of impurity levels.

Photoconductivity measurements made at 77°K are qualitatively similar for high-resistivity Fe-, Co-, and Ni-doped Ge crystals. Ionization energies deduced from impurity photoconduction thresholds in *n*- and *p*-type samples are consistent with the values quoted in Table I, except for *n*-type Fe-doped samples, for which photoconductivity studies indicate a somewhat deeper level, similar to *n*-type Co- and Ni-doped crystals. In general, *n*-type samples are more photosensitive than *p*-type samples, exhibit quenching effects and are slower in response to changes in light levels.

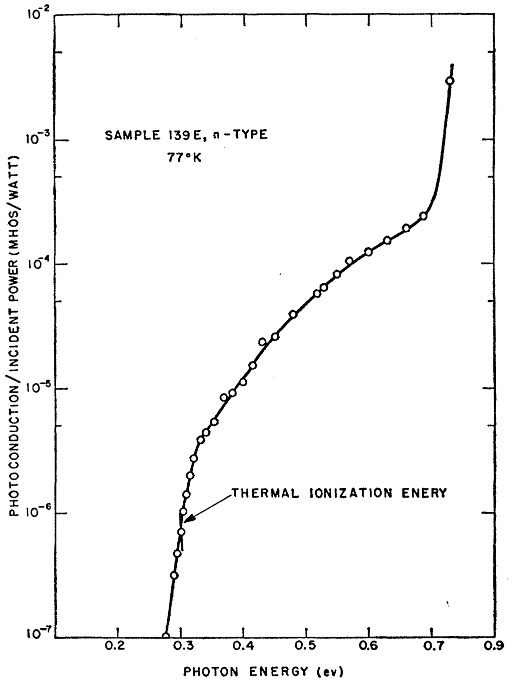

FIG. 8. Photoconductive spectrum of an *n*-type Ni-doped Ge crystal at 77°K (sample 139E).

TABLE I. Impurity levels and distribution coefficients (k_0)for iron, cobalt, and nickel in germanium. E_{vi} represents energy measured from the valence band to the impurity level in *p*-type samples; E_{ci} is measured from the impurity level to the conduction band in *n*-type samples.

	E_{vi} (ev)	E_{ci} (ev)	k_0
Fe	0.34	0.27	$<10^{-6}$
Co	0.25	0.31	$\sim 10^{-6}$
Ni	0.22	0.30	$\sim 2.3\times 10^{-6}$

It is tentatively assumed that Fe, Co, and Ni are substitutional impurities in the Ge lattice, each acting as a double acceptor giving rise to the energy levels quoted in Table I. Evidence that the impurity states are acceptors is direct for Ni and Co and is assumed for Fe because of similar atomic properties of Fe, Co, and Ni and the analogous photoconductive properties of crystals doped with Fe, Co, and Ni. No evidence that these impurities introduce more than two deep levels has been obtained.

Evidence for the double-acceptor model is not considered conclusive. It is possible that the two different levels observed for each of the transition metals studied are due to impurity atoms at two different types of sites at about the same concentration. The number of lattice imperfections in even the best crystals is probably sufficient to account for the observed solubility of Fe, Co, and Ni. Observed similarity of the impurity photoconductive spectra of *n*-type crystals may imply that the upper levels are due to structural defects or some other property common to Fe-, Co-, and Ni-doped crystals and independent of the atomic properties of the specific doping impurity.

Most of the uncertainty concerning the properties of Ge crystals doped with transition metals is related to their low effective distribution coefficients and the presence, in the purest metals available, of significant concentrations of high distribution coefficient impurities. Also, in samples dominated by high-ionization-energy impurities the carrier concentration at low temperatures decreases to very low values and it is difficult consistently to obtain homogeneous samples with well-behaved mobility. This problem has been particularly serious for Ni-doped samples. Uneven cooling of the ingot after crystallization, combined with a pronounced retrograde solid solubility could be in part responsible for this lack of homogeneity.